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Native Sources of Tanning Materials

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Most of the vegetable tannins used to tan our many kinds of leather we get from other countries. If we want to be independent of foreign supplies and have domestic tannins adequate to meet the critical needs of a national emergency, we will have to increase our production of new tannins, develop tannins from plants that can be grown as farm crops, and salvage more tannin from waste barks.

Tannins occur naturally in most plant materials, but relatively few plants that are rich in tannin are also adapted for cultivation just for tannin crops. Two native materials, canaigre and sumac, seem to be well suited for crop cultivation and are now being studied by the Department of Agriculture.

Canaigre, *Rumex hymenosepalus* Torr, belongs to the dock family. It is native to southwestern United States and northern Mexico. Its tuberous roots, which look somewhat like sweetpotatoes, are rich in tannin and have been used in tanning leather for centuries by the Mexicans and Indians. It is propagated by roots, root crowns, or seed. Canaigre planted in the fall grows during the winter and blooms in early spring. The top dies back in May or June. The roots remain dormant until fall, when they sprout again. Harvesting is usually done in July, August, or September. Under favorable conditions annual yields of about 10 tons of fresh roots to the acre can be expected.

Sandy, well-drained soils and dry climates in Texas, New Mexico, and Arizona are well adapted for growing canaigre. To assure good yields, irrigation is desirable. By selection of planting stock, strains of high yield and tannin content can be developed. Experimental plots have been successfully harvested with standard potato-digging equipment. Washing, shredding, and rapid air-drying 1 or 2 weeks after harvest insure roots that can be stored and shipped without spoilage. Harvested roots exposed too long in the air become hard and difficult to shred. Damaged roots mold readily.

Freshly dug canaigre roots contain 65 to 75 percent moisture. The tannin content of the moisture-free roots usually ranges from 20 to 40 percent. Some samples of wild roots have been found to contain more than 43 percent tannin. The roots also contain 8 to 20 percent sugar and 25 to 40 percent starch.

Two native strains have been observed. They differed in color, in tannin content, and in behavior in experimental studies of leaching.

The problems encountered in extracting tannin and making extracts of high commercial quality from canaigre roots differ greatly from those met in preparing tanning extracts from bark or wood. The starch in canaigre makes it impracticable and inefficient to extract coarse shreds countercurrently with hot water, in accord with the usual commercial practice as applied to barks. The swelling and gelatinization of the starch by hot water prevent effective extraction of the tannin. To overcome that difficulty, several laboratory-scale procedures were investigated. One gave promising results. The properly prepared canaigre was extracted in accordance with the countercurrent principle, by which water at 104° to 113° F. went on the spent material in the tail leach, moved forward through several lots, and came off as a concentrated head liquor from the finely divided fresh material in the head leach. Between each forward step the liquor and partly spent material were subjected to vigorous mixing at 104° to 113° F., followed by mechanical separation of liquid and solids. This procedure gave leaching efficiencies of 75 to 85 percent. For example, from 100 parts of canaigre roots containing 35.5 parts of tannin, 29.4 parts of tannin were recovered in the extracted liquor.

The sugars present in canaigre roots are soluble and are extracted with the tannin by water. When the extracted liquors containing tannin and sugars and other nontannin substances are concentrated, the tanning extracts produced are low in purity because of the sugars present. We raised the purity of the extracts by removing the sugars by fermentation, using specially isolated bacteria. Several strains of *Aerobacter aerogenes*, obtained from canaigre roots and the soil in which canaigre grows, made effective growth and destroyed the sugars in canaigre liquors without material loss of tannin. The principal products of this fermentation are 2,3-butanediol, acetoin, and ethyl alcohol.

Comparison of analyses of powdered canaigre extracts made from unfermented and fermented canaigre liquors shows that by fermentation of liquors the quality of tanning extract can be greatly improved. For example, in one case the sugar content of an extract was lowered from 22.9 to 0.7 percent and the nontannin from 44.0 to 28.7 percent, while the tannin content was raised from 49.7 to 62.1 percent and the purity from 53 to 68.4.

By the fermentation procedure, we got canaigre extracts that compare acceptably with some of the best commercial tanning extracts, such as powdered chestnut (with a tannin content of 61.3 percent and a purity of 66.3) and ordinary solid quebracho extract (with a tannin content of 68.5 percent and a purity of 87.5).

In laboratory-scale extractions that used aqueous-organic solvent mixtures, those containing acetone or isopropyl alcohol gave best tannin recovery. Both were more efficient than water and had the further advantage that when the solvents were used in proper concentrations starch did not interfere in the extraction. Because of the costs of the solvent, fire hazards, and recovery problems, however, further study and an analysis of costs are needed to establish the economic feasibility of their use.

In laboratory tests, canaigre extracts have been successfully used both alone and blended with other tannins for the tanning of good-quality leathers of the sole-leather type.

Several processes for the preparation of tanning extracts from canaigre are being studied on a pilot-plant scale. For each process, that entails the correlation of drying, grinding, leaching, and clarification operations so as to obtain an integrated process. Also to be determined are the engineering and economic factors that govern the choice of commercial equipment. Both batch and continuous leaching are being studied. The most promising results have been obtained by fine grinding of the dried roots. Tannin yields are enhanced by the addition of less than 20 percent of an organic solvent to the leaching water, but its economic desirability has not been fully evaluated.

Sumac, a shrub that grows wild in this country, has long been known as a source of tanning and dyeing material. Its tannin is not well adapted for general use in tanning heavy leather. Its present use—to make lightweight leathers—might well be expanded, however, so as to help meet the demand for additional domestic tannins.

Sumac tannin, obtained from the leaves, is used as ground leaf or as a liquid extract. Tanners of lightweight leathers like it because it produces soft, durable, light-colored leathers of desirable feel.

Frequently a product of low quality is obtained because woody stalks low in tannin are collected with the leaves, deep piling during drying causes spoilage, or exposure of the leaves to dew or rain causes loss of tannin. The correction of such unsatisfactory practices will aid in obtaining a commercially acceptable product, and tanners will have less justification for their preference for the imported Sicilian sumac, *Rhus coriaria.*

Workers in the Department have found that sumac leaves of acceptable tannin content and commercial quality can be produced from domestic species if correct procedures are used in harvesting and drying.

The possible economical development of sumac for tannin, therefore, deserves consideration. The development involves the cultivation of high-quality sumac strains as farm crops and the mechanical harvesting and handling of the product by improved methods. Investigations are now in progress.

The three domestic sumacs that seem most promising for cultivation as tannin crops are the dwarf sumac (*Rhus copallina*), white sumac (*Rhus glabra*), and staghorn sumac (*Rhus typhina*). All have compound leaves, which average 32.5, 27.3, and 25.6 percent, respectively, of tannin on a moisture-free basis. They will grow on dry and sometimes rocky soil. Dwarf sumac has winged growths along the midribs between the leaflets and black specks on new-growth stalks. White sumac has smooth stalks and a bluish-white bloom, like the bloom on plums, which covers the stalks and the underside of the leaflets. Staghorn sumac has a hairy growth along the stalks and leaf midribs.

Sumac can be grown satisfactorily from seed or root stock, but roots must be handled promptly or they will die. No seed is yet available that can be guaranteed to produce high-tannin plants. Propagation by means of root stock is slow in getting large acreages under cultivation, but it has the advantage that high-quality strains can be maintained by its use. Rich soil produces luxuriant growth, but then the leaves are low in tannin and the yield of tannin to the acre is not greatly increased.

A survey of sumac that grew wild over 12,000 square miles in southern Virginia indicated that about 43,000 long tons of dry sumac leaf could be collected there annually.

Ira D. Clarke, A. F. Sievers, and Henry Hopp, and I have studied eight species of sumac native to the eastern and southern parts of the United States to determine tannin content and abundance. The results of our investigations are given in the Department Technical Bulletin No. 986, *Tannin Content and Other Characteristics of Native Sumac in Relation to Its Value as a Commercial Source of Tannin.* (1949.)

We found that leaves, leaflets, and flowers of sumac were high in tannin and that all other parts of the plant were low in tannin and would lower the quality of the leaf product if mixed with it. In a statistical study of the effects of genetic and environmental factors on composition, we learned that leaves of male plants of *Rhus copallina* contained an average of 3.3 percent more tannin than those of female plants; that leaves of *Rhus copallina* and *Rhus glabra* that grew in partial shade averaged 2.8 percent less tannin than leaves of similar plants growing in full sunlight; and that date of collection influenced tannin content, there being an average decrease in tannin of 0.047 percent a day during the summer.

Yields of leaves calculated from small plots of plants 1, 2, and 3 years old indicate that ½ to 3 tons of dry leaves can be had from an acre under varying conditions. More data are needed on methods of harvesting applied successively for several seasons to plots of an acre or more.

Sumac leaves dried rapidly at ordinary temperatures with good ventilation do not change in composition. They produce good, light-colored leather. Slow drying at ordinary temperatures, caused by poor aeration or high humidity, means a loss of nontannin material, principally sugar, but does not change the amount of tannin. Such partly decomposed leaves produce dark leather. Drying at 212° F. results in a slight loss of tannin and sugar, but the product produces good, light-colored leather.

In a commercial tanning test on more than 330 dozen sheepskin skivers, all three domestic species produced satisfactory leather that was approximately equal to that produced by Sicilian sumac.

F. P. Luvisi and Ira D. Clarke, at the Eastern Regional Research Laboratory, learned that a temperature of 212° F. was most efficient for extraction for the determination of tannin. They also found that heat up to 212° F. had only a slight effect on dry leaves, but that leaves were altered by steeping in water, apparently by a change of tannin into nontannin. Both temperature and time of steeping were factors.

Ivan L. Boyd, in comprehensive research on sumac at Iowa State College in cooperation with the Soil Conservation Service, found that four native species—*Rhus glabra, R. copallina, R. typhina,* and *R. aromatica*—had possibilities for cultivation as sources of tannin and, because of their spreading, shallow root systems, were valuable in preventing soil erosion. Of these, *R. glabra* was the most promising for southeastern Iowa. Propagation of the species by root cuttings gave a survival rate of 10 to 82 percent. Seed from the four species treated with concentrated sulfuric acid gave an average germination of 13 percent. Better germination was obtained with seed selected from clones yielding a high percentage of viable seed. Seedlings from *R. glabra* and *R. typhina* reach harvesting size in about 3 years. The tannin content of leaves increases each year in seedlings but seldom exceeds that of the adult clone. It is increased by deblossoming the plant and is lowered by growth in shade. Three-year-old seedling plants of the four species gave yields at the following rates per acre: *R. aromatica,* 416 pounds; *R. glabra,* 592 pounds; *R. copallina,* 975 pounds; and *R. typhina,* 2,250 pounds.

E. L. Barger and J. M. Aikman, of Iowa State College, developed a power-driven harvester that was suitable for harvesting sumac from both wild and cultivated stands. Under favorable conditions about 3 tons of green leaf could be harvested a day, an amount equal to what 10 men could harvest by hand in a day. Tests were also conducted on drying and mechanical separation of leaves from woody stalks.

In the development of sumac as a domestic tannin crop, machine methods for harvesting, drying, and separation of leaves from stems reduce labor costs and aid in meeting competition from sumac from foreign countries where labor costs are low.

The recovery of tannin from available supplies of unused and waste barks could aid materially in meeting the present shortage in domestic tannins. Among the barks that might be used are Florida scrub oak (*Quercus laevis*), with 10 percent tannin; eastern hemlock (*Tsuga canadensis*), 12 percent; western hemlock (*Tsuga heterophylla*), 15 percent; Douglas-fir, (*Pseudotsuga taxifolia*), 10 percent; Florida mangrove (*Rhizophora mangle*), 31.5 percent; and a mixture of oaks from the Tennessee Valley, which would probably average about 8 percent tannin. Although of acceptable tannin content, some of the barks offer no promise as economical sources of tannin.

Bark of western hemlock, one of the largest undeveloped sources, represents a potential annual supply of about 35,000 tons of 100-percent tannin. It is not too promising, however, because the practice of floating logs downstream causes a loss of about one-half of the bark tannin and salt contamination of the bark on logs floated in salt water.

Florida mangrove bark is inaccessible and costly to collect. It probably would not yield more than 1,000 tons of 100-percent tannin annually for 5 years.

The barks of the Florida scrub oaks might be recovered by hogging the logs and branches and mechanically separating the bark from the wood by air flotation, as described by H. N. Calderwood and W. D. May, at the Florida Engineering and Industrial Experiment Station. The bark would be used as a source of tannin and the wood for paper pulp. The bark might furnish as much as 5,000 tons of 100-percent tannin annually for 20 years.

L. F. Bailey and W. H. Cummings, of the Tennessee Valley Authority at Norris, Tenn., found that mixed oak slabs could be extracted to yield about 3,000 tons of 100-percent tannin a year.

The Lake States region has supplies of hemlock bark which, if salvaged, should yield around 17,000 tons of 100-percent tannin annually. The high cost of peeling and collection raises a question, however, as to the economical feasibility of utilizing this bark to make tanning extract.

Douglas-fir bark, now being investigated at the Oregon Forest Products Laboratory, appears to have promise. The investigators found tannin contents of 7.6 to 18.3 percent, and estimated that the average tannin content would be about 10 percent. They found that the bark also contained an average of 7 percent of waxes and 5 percent of dihydroquercetin. They estimate a potential annual tannin recovery equal to more than 150,000 tons of 100-percent tannin. If such a quantity of fir bark tannin could be produced economically, it would aid greatly in solving this country's tanning material shortage. However, the tanning properties of fir bark tannin require further study to determine its suitability for making various types of leather.

The vegetable tannins most commonly used in making leather are water-soluble materials obtained from barks, woods, leaves, and fruits—for example, the barks of oak, hemlock, wattle, and mangrove, the woods of quebracho and chestnut, the leaves of sumac and gambier, and the fruits of valonia oak, myrobalan, tara, and divi divi. Of these, the one most extensively used in our leather industry is the tannin from quebracho wood, which we import from Argentina and Paraguay as solid extract. Second is the tannin from chestnut wood, which is produced domestically but may be exhausted soon because blight has killed nearly all commercially important stands of chestnut.

Fifty years ago most of the leather produced in the United States was tanned with tannins from oak and hemlock bark. Today only a limited amount is produced from them. Small amounts of tanning extracts are made from domestic supplies of sumac leaves and pecan shells. All other vegetable tannins are imported.

Accurate data on our use of tannin are not available, but some idea of the amounts can be obtained from import figures and estimates of domestic production. From 1940 to 1949, the United States consumed annually an average of about 125,000 tons of 100-percent tannin; more than 70 percent of it was imported. Quebracho tannin, from South America, constituted nearly 70 percent of the foreign tannin group and more than 50 percent of the total consumption. Chestnut wood tannin accounted for about 95 percent of the domestically produced tannin and about 25 percent of the total consumption. Tannin from wattle bark, imported principally from Africa, held third place. Mangrove bark tannin, from Africa and South America, was fourth.

Drillers of oil wells have discovered that quebracho tanning extract, treated with caustic alkali, helps in regulating the viscosity and consistency of drilling muds. Several thousand tons of extract are used annually for the purpose. To relieve that added demand, substitute extracts or other materials suitable for the purpose are being sought.

The essentiality of vegetable tannins in the manufacture of leather is illustrated in figures for leather production in the United States in 1949 (in millions):

Hides or skins:	*Vegetable-tanned*	*Mineral-tanned*	*Total tanned*
Cattle	8.2	15.2	23.4
Sheep and lamb	8.5	20.3	28.8
Calf and kip	1.0	9.1	10.1
Goat and kid		34.7	34.7

The mineral-tanned leathers were tanned principally with chrome but included alum and all other mineral tannages and also mineral-tanned leathers that were retanned with vegetable tannins.

Vegetable tanning materials were used for tanning approximately 35 percent of the cattle-hide leather, 30 percent of the sheepskin and lambskin leather, and 10 percent of the calfskin and kip leather.

Cattle hides, when vegetable-tanned in their original thickness, yield heavy, thick, firm leathers, which are especially adapted for use as shoe soles, harness, luggage, and belting. Leathers of those types take more tannin than do the lightweight, soft, flexible leathers used for shoe uppers, gloves, garments, and fancy leather goods.

One tanner uses a blend of vegetable tannins containing 51.2 pounds of 100-percent tannin to produce 100 pounds of air-dry sole leather from steer hides. A tanner of light leather, on the other hand, to produce 100 pounds of calfskin and sheepskin leathers uses, respectively, only 36 and 40 pounds of 100-percent quebracho tannin. Heavy leathers are tanned principally with vegetable tannins. For light leathers, mineral tannages, such as chrome or alum, are commonly used. The properties of leather differ according to the tanning materials. For some uses, mineral-tanned leathers are preferred; for others, vegetable-tanned leathers are better. Some synthetic tannins are often used in light-leather tannages. They have also been used in some heavy-leather tanning, but their prices are materially higher than those of vegetable tannins.

Present domestic sources of tannin are chestnut wood, oak and hemlock barks, sumac leaves, and pecan shells.

Most of the domestic tannin, probably more than 95 percent, is obtained from the wood of the American chestnut, *Castanea dentata*. It is quite generally known, as I said before, that the trees that constituted the commercial stands of chestnut in the United States are being killed by blight, caused by a parasitic fungus, which was brought into the country on Japanese chestnut trees planted on Long Island about 1893. By 1904 native chestnuts were dying. Progress has been made in developing blight-resistant chestnut trees by G. F. Gravatt, Jesse O. Diller, and Russell B. Clapper, of the Bureau of Plant Industry, Soils, and Agricultural Engineering.

Ira D. Clarke, E. T. Steiner, and R. W. Frey, of the Bureau of Agricultural and Industrial Chemistry, studied the tannin contents of the blight-resistant Chinese chestnut, *Castanea mollissima*, and found that trunk wood from trees 16 and 25 years old contained 8.0 and 12.0 percent tannin, respectively, compared with 8.4 percent for 14-year-old American chestnut. Although the tannin content of blight-resistant chestnuts compares favorably with that of the native chestnut, because of the long time required to produce commercial stands, there appears to be no prospect for the development of a domestic tannin supply from this source.

In any study of the possibilities for the economical development and utilization of available bark supplies, several factors need to be considered—the quantities available, accessibility, tannin content, possible byproducts, and the costs of bark, extract production, and transportation. Of the barks investigated, the oaks from Florida and the Tennessee Valley, the hemlock from the Lake States area, and the fir from Oregon and Washington appear to have promise. The bark from western hemlock would also be a promising source of tannin if it could be salvaged from logs that have not been floated.

The production of tannin from farm crops has many desirable features. It offers a new crop at a time of farm surpluses. The production of canaigre and sumac will furnish two types of tannin that will be available for blending with other tannins. Sumac will be adapted for light-leather tannage and for many purposes could replace quebracho. Canaigre will be a root crop that can be harvested with available farm machinery. Associated with the canaigre tannin will be starch and sugar, byproducts which may be used for production of fermentation products. Canaigre crops can be largely expanded or curtailed to meet rapidly changing demands.

The ability of this country to provide a major part of the vegetable tanning materials that it needs for the manufacture of leather depends on the successful completion of investigations now under way. We can probably best attain this objective by a combination of two lines of activities—one, the development of economical procedures for the salvage and utilization of available supplies of oak, hemlock, and fir barks; the other, the large-scale cultivation and production of canaigre, sumac, and other tannin-bearing plants as farm crops.

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